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I: QUIET MIDLATITUDE CONDITIONS

Research and development rept.

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By

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Two long-standing problems in the atmospheric sciences have been the correct modeling of the ion chemistry in the earth's atmosphere and the proper determination of the ion species and densities through in situ measurements. Comparison between experimental data and simultaions of those data by computer modeling of atmospheric chemistry is a means of validating the computer code as well as indicating which processes are in need of further study. The DAIRCHEM computer code is used here to simulate data taken in the midlatitude D region during quiet conditions. Comparison between the total positive ion

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20. ABSTRACT (cont)

density profile derived from rocket measurements and the one computed by the code shows very good agreement in the 30 to 90 km range, with the exception that the simulated ion density profile is of somewhat smaller magnitude than the experimental one in the 60 and 75 km region. Such a discrepancy is only partially explained by the uncertainties in the ionization rate of NO due to Lyman alpha radiation. Comparison between the measured and the computed electron density profiles shows that the measured profile is consistently of a smaller magnitude than the computer profile in the 65 and 85 km range. We interpret this discrepancy as a deficiency in the modeling of the negative ion chemistry. Also, this deficiency is probably the main cause of the disparity between the total positive ion density profiles in the corresponding altitude range. The authors feel that the positive ion chemistry is reasonably well understood and that this section of the DAIRCHEM code may be considered validated. The negative ion chemistry needs to be studied further. Specifically, alternate electron attachment/detachment processes should be considered, as well as an as-yet-undetermined, possibly very massive, negative species which may affect the ion recombination rates. Successful modeling of the D region under naturally occurring conditions is one means of validating the computer codes which are used as input for Army communications systems codes and nuclear weapons effects codes.

SUMMARY

Experimental data from rocket measurements taken in the quiet, daytime D region and simulations of these data by the DAIRCHEM computer code are compared. The purpose is to validate the computer code and to identify those physical processes that need further study.

The direct comparison of simulated and experimental data is shown graphically. It is important to note that no data have been normalized. The total positive ion density profiles show good agreement over the 30 to 90 km region with the exception of the 60 to 75 km span. Possible variations in the absorption of Lyman alpha radiation could account for part of the discrepancy, although it is felt that uncertainties in the formation of negative ions and the total negative ion and electron densities are the cause. Qualitative agreement between predictions of the detailed positive ion composition and in situ mass spectrometric measurements indicate that the positive ion chemistry is being correctly modeled. The computed dominant positive and negative ions are listed as a function of altitude in a table which serves as a guide when comparing these results with other measurements or theoretical calculations.

Comparison of the simulated and experimental electron density profiles shows that the experimentally derived values consistently lie below the predicted ones in the 60 to 85 km region. Mass spectrometer measurements of negative ions (currently available only above 70 km) show little agreement with current predictions in the 70 to 90 km range. These discrepancies indicate that there are electron attachment mechanisms and one or more negative species, possibly small particulates, which are not being correctly modeled.

CONTENTS

INTRODUCTION

The Air Chemistry (AIRCHEM) computer code[1] has been developed to simultaneously solve a large number of stiff, time-dependent, differential equations[2] and thus correctly describe the ion chemistry associated with the nuclearly disturbed atmosphere.[3] A variation of this code, D Region Air Chemistry (DAIRCHEM), has also been developed to model the chemistry of the ionospheric region under both quiet and naturally disturbed conditions.[4] The plan is to compare the predictions of the DAIRCHEM code against experimental data. Reasonable agreement between the measured data and simulations of that data by the DAIRCHEM code serves to validate the code, whereas disagreement indicates which atmospheric processes need further study. Validation of the DAIRCHEM code increases the level of confidence in the AIRCHEM code's predictions for the nuclearly disturbed atmosphere and its potential effects on Army systems.

The case studied here is the daytime, quiet, midlatitude D region. A series of coordinated measurements was made from Wallops Island (37.8° N, 75.5° W) for an extended period of time which covered both quiet and disturbed days. The data selected for comparison were taken on 31 January 1972, a quiet day with no anomalous D region radio absorption. Two rocket flights at 12:30 and 13:05 local time (solar zenith angles of 55° and 58°,

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[1]E. L. Lortie, M. D. Kregel, and F. E. Niles, 1976, "AIRCHEM: A Computational Technique for Modeling the Chemistry of the Atmosphere," BRL Report 1913 (AD A030157)

[2]T. P. Coffee, J. M. Heimerl, and M. D. Kregel, "A Numerical Method to Integrate Large Stiff Systems of Ordinary Differential Equations," submitted to BRL for publication

[3](see for example) J. M. Heimerl and F. E. Niles, 1978, "BENCHMARK-76: Model Computations for Disturbed Atmospheric Conditions III. Results for Selected Excitation Parameters at 60 km," BRL Technical Report ARBRL-TR-02051 (and references therein).

[4]D. W. Hoock and M. G. Heaps, 1978, "DAIRCHEM: A Computer Code to Model Ionization/Deionization Processes and Chemistry in the Middle Atmosphere," Atmospheric Sciences Laboratory Internal Report, White Sands Missile Range, NM

respectively) provided independent experimental measurements of the electron and total positive ion densities.[5,6,7]

COMPARISONS OF EXPERIMENTAL DATA WITH THE DAIRCHEM SIMULATIONS

The important sources of ionization for the D region are X-rays, Lyman alpha radiation (Lyα) and galactic cosmic rays (GCR). The ion-pair production rates (q) used in the computations[8] are shown in figure 1; the sources were not directly monitored during the rocket measurements. Because 31 January was a quiet day, the X-ray flux was not large, and the direct ionization of NO by Lyα was the largest source of electrons throughout the D region. Due to the rapid attenuation of Lyα by O_2,

the dominant source of ionization near 65 km and lower becomes the GCR background. The source of ionization does affect the type of positive ion which is produced. During quiet periods, NO^+ is the most abundant ion initially produced throughout the D region. At 65 km and below, the initially produced ions are N_2^+, O_2^+, N^+, and O^+, in that order;[9] but due to rapid charge exchange and ion-atom interchange processes, the effective ion production rate is approximately 0.8 O_2^+ and 0.2 NO^+ ions per ion pair. The effects on the positive ion chemistry will be discussed in the next section.

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[5]L. C. Hale, 1974, "Positive Ions in the Mesosphere," COSPAR Methods of Measurements and Results of Lower Ionospheric Structure, K. Rower, ed., 219-235, Akademie-Verlag, Berlin. See also J. D. Mitchell, "An Experimental Investigation of Mesospheric Ionization," Ionospheric Research Scientific Report 416, Pennsylvania State University, 27 June 1973; and T. W. Lai, "Electron Collection Theory for a D-Region Subsonic Blunt Electrostatic Probe," Ionospheric Research Scientific Report 424, Pennsylvania State University, 20 May 1974

[6]L. G. Smith and K. L. Miller, 1978, "The Measurement of O_2 Number Density by Absorption of Lyman Alpha," J Geophys Res, 79:1965-1968

[7]E. A. Mechtly, 1974, "Accuracy of Rocket Measurements of Lower Ionospheric Electron Concentrations," Radio Sci, 9:373-378. See also Progress Report 73-1, p. 62ff, Research in Aeronomy October 1, 1972 - March 31, 1973, edited by Belva Edwards, University of Illinois, Urbana, Illinois, 1973

[8]I. Chidsey, 1978, "SOURCE: A FORTRAN-IV Subroutine Package that Models Several Naturally Occurring Energy Inputs to the Mesosphere," BRL Technical Report, ARBRL-TR-02093

[9]F. Gilmore, as quoted in table 6 in B. F. Myers and M. R. Schoonover, "Electron Energy Degradation in the Atmosphere: Consequent Species and Energy Densities, Electron Flux, and Radiation Spectra," DNA 3513T, 3 January 1975
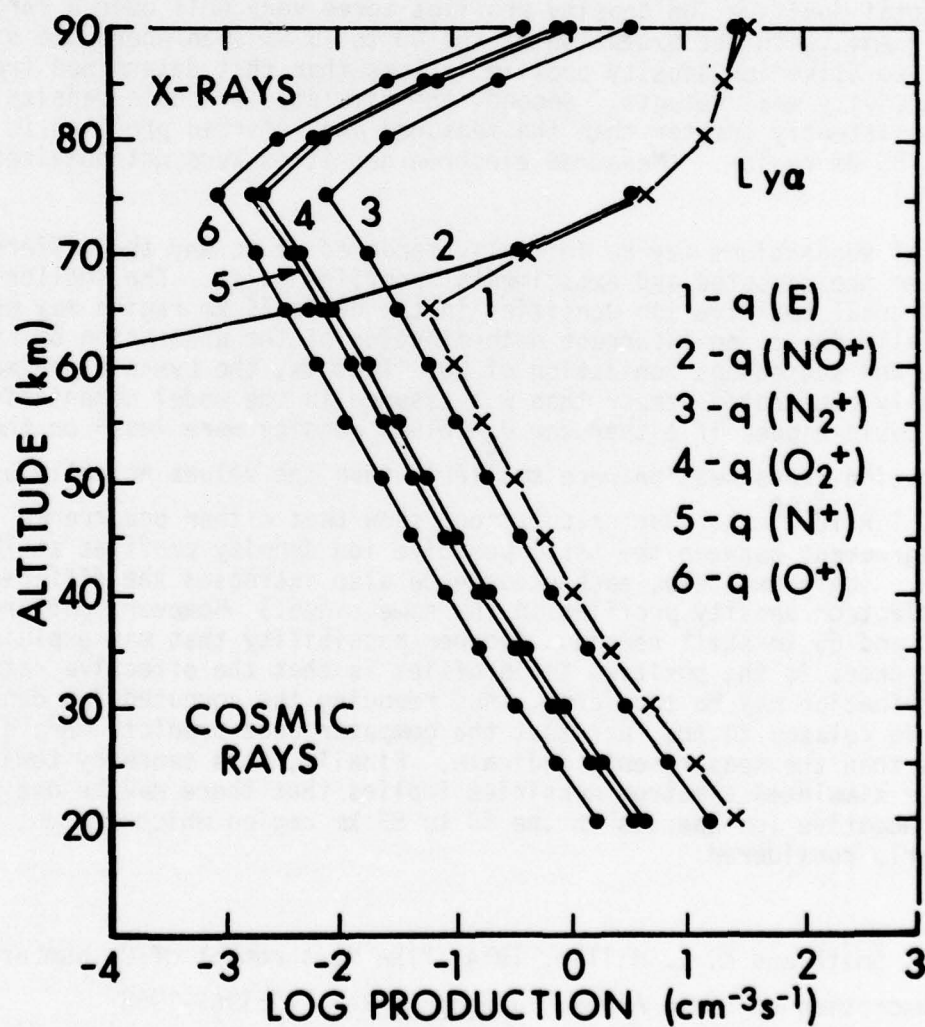
Figure 1. The production rates for electrons and five positive ions as a function of altitude. Direct ionization of NO by Lyman alpha radiation far exceeds the X-ray production above 65 km. Cosmic ray ionization is the source below 65 km.

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The electron and total positive ion density profiles computed by using ion pair production rates from figure 1 are shown as circles in figure 2. (Note that the upper scale for the positive ions has been adjusted to the right.) The computed electron densities and total positive ion densities are essentially equal to one another above 65 km. Also shown in figure 2 for comparison are the total positive ion density profile (derived from blunt probe conductivity data), the inferred electron densities from the same data, and the measured electron density profile (combined probe and propagation experiment). We emphasize that the profiles have been simply overlaid; no data have been normalized.

Two general points should be noted when the profiles are compared. First, the total positive ion density profiles agree very well over a large altitude range, with the exception of the 60 to 75 km span where the simulated total positive ion density profile is less than that determined from the conductivity measurements. Second, the simulated electron density profile is consistently greater than the measured and inferred profiles in the 60 to 85 km region. (Measured electron densities were not obtained below 60 km.)

Several suggestions may be initially tendered as to why the differences between the computed and experimental profiles exist. The smaller simulated total positive ion densities in the 60 to 75 km region may be partially due to an incorrect determination of the absorption of Lyman alpha and subsequent ionization of NO. That is, the Lyman alpha may have actually penetrated deeper than was assumed in the model computation. This could happen if either the O_2 column density were less[6] or the O_2 absorption cross section were smaller[10] than the values actually used, i.e., $1 \times 10^{-20} cm^2$. Our calculations show that either occurrence improves the agreement between the total positive ion density profiles at 70 and 75 km. (Unfortunately, each occurrence also increases the differences in the electron density profiles in the same range.) However, differences at 60 and 65 km still remain. Another possibility that may explain the differences in the positive ion profiles is that the effective rate of recombination may be too large, thus reducing the computed ion densities. This is related to the fact that the computer code predicts more electrons than the measurements indicate. Finally, this tendency toward larger simulated electron densities implies that there may be one or more negative ion species in the 60 to 85 km region which are not being properly considered.

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[6]L. G. Smith and K. L. Miller, 1974, "The Measurement of O_2 Number Density by Absorption of Lyman Alpha," J Geophys Res, 79:1965-1968

[10]J. H. Carver, H. P. Gies, T. I. Hobbs, B. R. Lewis, and D. G. McCoy, 1977, "Temperature Dependence of the Molecular Oxygen Photoabsorption Cross Section Near the H Lyman Alpha Line," J Geophys Res, 82:1955-1960
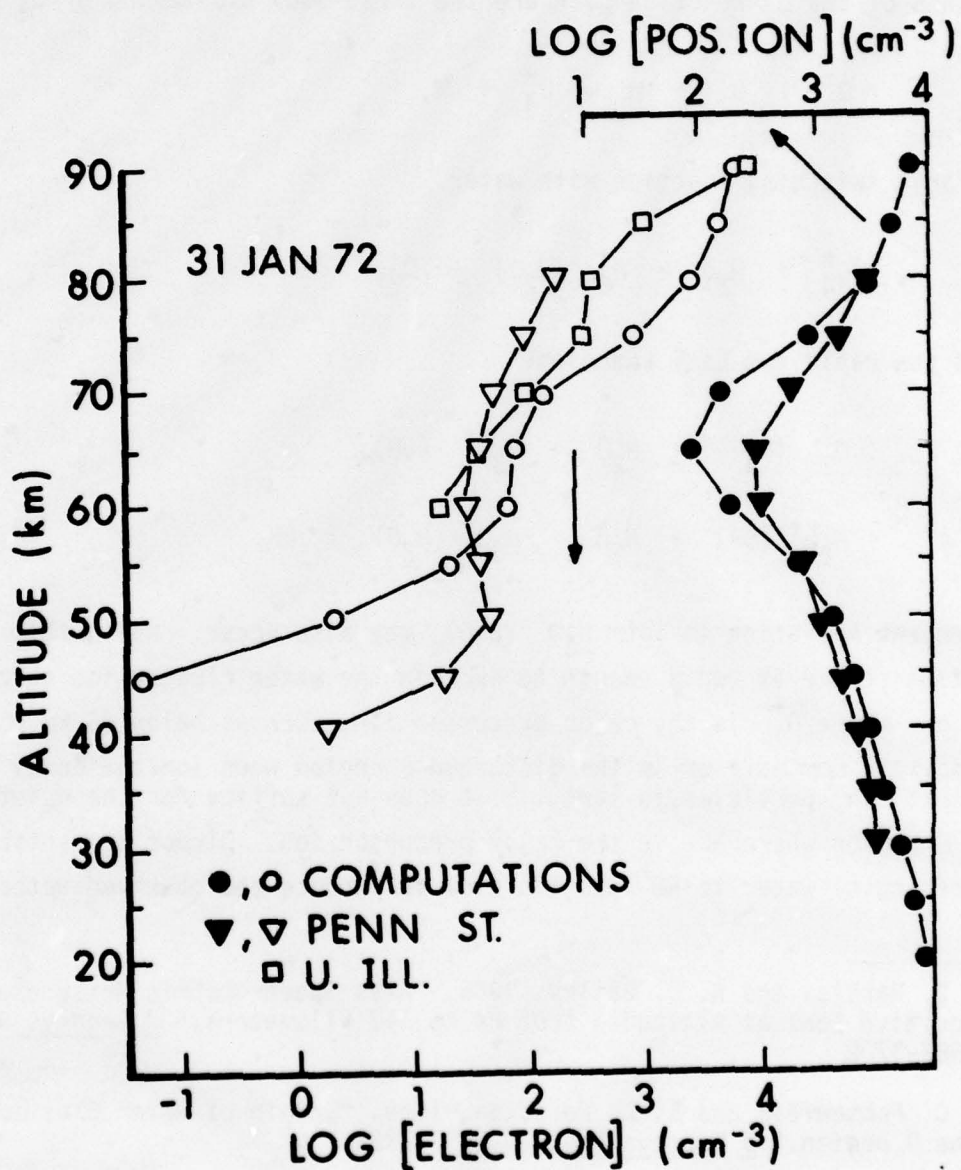
Figure 2. Open symbols are the electron density profiles (bottom scale). Measurements were made by the Pennsylvania State University Group (ref 5) and the University of Illinois Group (ref 7). Solid symbols are the total positive ion profiles (top scale). Measurements were made by the Pennsylvania State University Group (ref 5).
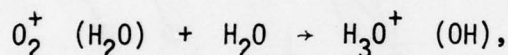
POSITIVE ION CHEMISTRY

The measurement[11] more than a decade ago of water cluster ions in the D region substantially revised our understanding of that portion of the ionosphere. Subsequent laboratory studies[12,13] showed that pathways do exist for converting O_2^+ and NO^+ ions to water cluster ions. The essential points of the O_2^+ reaction path are the three-body clustering of O_2^+ with O_2

$$O_2^+ + O_2 + M \rightarrow O_4^+ + M,$$
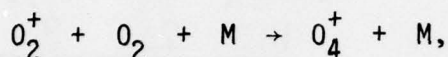
a rapid switching reaction with water

$$O_4^+ + H_2O \rightarrow O_2^+ (H_2O) + O_2,$$
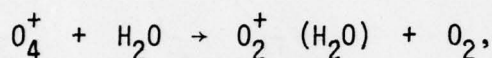
and the rapid two-body reactions

$$O_2^+ (H_2O) + H_2O \rightarrow H_3O^+ (OH),$$

$$H_3O^+ (OH) + H_2O \rightarrow H_3O^+ (H_2O) + OH.$$

Subsequent hydration to form $H_3O^+ (H_2O)_n$ may also occur. While this reaction scheme is rapid enough to explain the water cluster ion concentrations where O_2^+ is the major precursor ion, such as below 65 km where cosmic rays dominate or in the disturbed D region when ionization by precipitating particles is large,[14] it does not suffice for the quiet time D region where NO^+ is the major precursor ion. Direct sequential clustering of water to NO^+ was too slow to produce the observed water

[11]R. S. Narcisi and A. D. Bailey, 1965, "Mass Spectrometric Measurement of Positive Ions at Altitudes from 64 to 112 Kilometers," J Geophys Res, 70:3687-3700

[12]F. C. Fehsenfeld and E. E. Ferguson, 1969, "Origin of Water Cluster Ions in the D Region," J Geophys Res, 74:2217-2222

[13]F. C. Fehsenfeld, M. Mosesman, and E. E. Ferguson, 1971, "Ion Molecule Reactions in an O_2^+ - H_2O System," J Chem Phys, 55:2115-2119

[14]G. C. Reid, 1972, "The D Region During PCA Conditions," Magnetosphere Ionospheric Interactions, K. Folkstad, ed., 39-46, Universitets-forlaget, Oslo

cluster densities. More rapid switching reactions have been proposed[15,16] of the type

$$NO^+ + N_2 + M \rightarrow NO^+ (N_2) + M,$$

$$NO^+ (N_2) + CO_2 \rightarrow NO^+ (CO_2) + N_2,$$

$$NO^+ (CO_2) + H_2O \rightarrow NO^+ (H_2O) + CO_2,$$
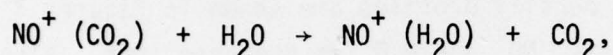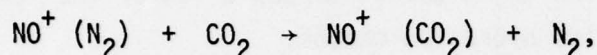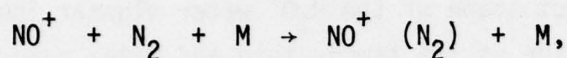
with a similar sequence until the third hydrate is produced. The third hydrate then undergoes a rapid two-body reaction with water

$$NO^+ (H_2O)_3 + H_2O \rightarrow H_3O^+ (H_2O)_2 + HNO_2,$$

and the hydronium ion sequence is entered.[17,18]

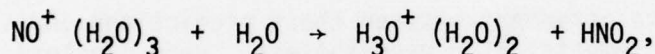Repeated rocket measurements over a wide variety of latitudes and seasons have shown that the hydronium ion clusters $H_3O^+ (H_2O)_n$ begin to rapidly

[15]F. E. Niles and J. M. Heimerl, 1972, "Association, Switching and Re-arrangement for Positively Charged Cluster Ions in the Upper Atmosphere, I: Qualitative Description," BRL Report 1595

[16]J. M. Heimerl, J. A. Vanderhoff, L. J. Pucket, G. E. Keller, and F. E. Niles, 1972, "Association, Switching and Rearrangement for Positively Charged Cluster Ions, II: Applications at 80 km," BRL Report 1605

[17]G. C. Reid, 1976, "Ion Chemistry in the D Region," Advances in Atomic and Molecular Physics, 12:375-414, Academic Press, New York

[18]G. C. Reid, 1977, "The Production of Water-Cluster Positive Ions in the Quiet Daytime D Region," Planet Space Sci, 25:275-290

decrease in density above about 75 to 85 km.[11,19-21] The main reason is that the clustering sequence involves several three-body reactions with major constituents and therefore rapidly decreases in efficiency with increasing altitude. The exact shape of the H_3O^+ water cluster ion profile is also somewhat a function of the temperature and water vapor profiles. Above 75 to 85 km, one might expect to see a few of the "early" clusters in the NO^+ and O_2^+ ion hydration chains.

The simulated positive ion density profiles are shown in figures 3 and 4 for ions having, respectively, NO^+ and H_3O^+ as the core ions. Also shown is the predicted total positive ion density profile. As expected, the computer code predicts that NO^+ and its first two water clusters, along with the intermediate cluster $NO^+ (CO_2)$, dominate the upper D Region. There is good qualitative agreement between these predictions and several mass spectrometric measurements;[19-22] nevertheless, these clusters are weakly bound and therefore subject to collisional breakup from the in situ rocket measurement techniques. Figure 4 shows the computed density profiles for the H_3O^+ hydrates. Above 65 km, entry to the hydronium ion chain is through NO^+ producing $H_3O^+ (H_2O)_2$, while below 65 km, entry is through O_2^+ producing $H_3O^+ (H_2O)$. The code predicts that clustering to heavier hydrates will be important below 75 km. Again, the comparison with mass spectrometric measurements gives good qualitative agreement.

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[11]R. S. Narcisi and A. D. Bailey, 1965, "Mass Spectrometric Measurements of Positive Ions at Altitudes from 64 to 112 Kilometers," J Geophys Res, 70:3687-3700

[19]D. Krankowsky, F. Arnold, H. Weider, J. Kissel, and J. Zähringer, 1972, "Positive Ion Composition in the Lower Ionosphere," Radio Sci, 7:93-98

[20]R. S. Narcisi, A. D. Bailey, L. E. Wlodyka, and C. R. Philbrick, 1972, "Ion Composition Measurements in the Lower Ionosphere During the November 1966 and March 1970 Solar Eclipses," J Atmos Terr Phys, 34:647-658

[21]A. Johannessen and D. Krankowsky, 1974, "Daytime Positive Ion Composition Measurement in the Altitude Range 73 - 137 km above Sardinia," J Atmos Terr Phys, 36:1233-1247

[22]F. Arnold and D. Krankowsky, "A New Concept for the D Region Ion Chemistry as Inferred from a Mass Spectrometer Measurement," paper presented at International Symposium on Solar-Terrestrial Physics, COSPAR, Sao Paulo, Brazil, 1974

Figure 3. Computed positive ion density profiles for species that have NO^+ as their core ion. The total positive ion profile is given by the heavy curve marked "T."
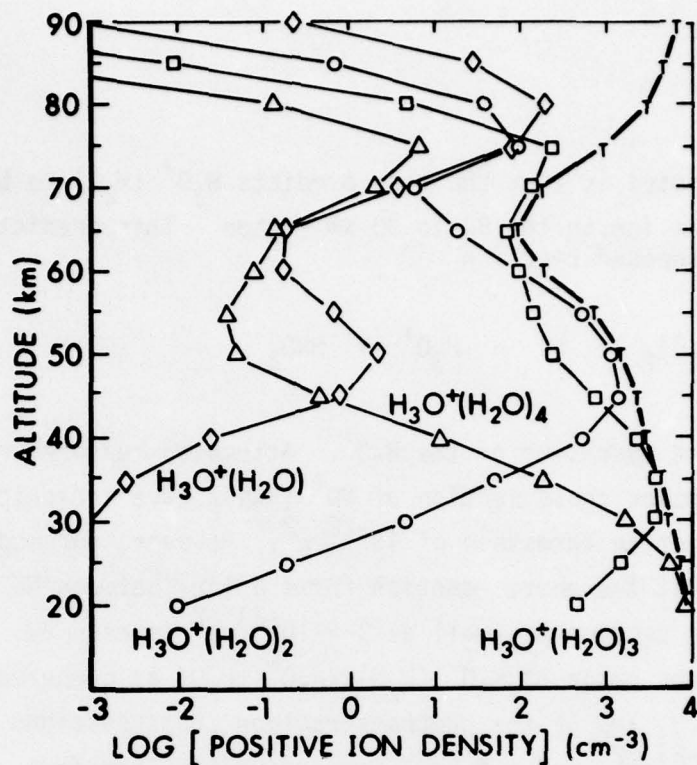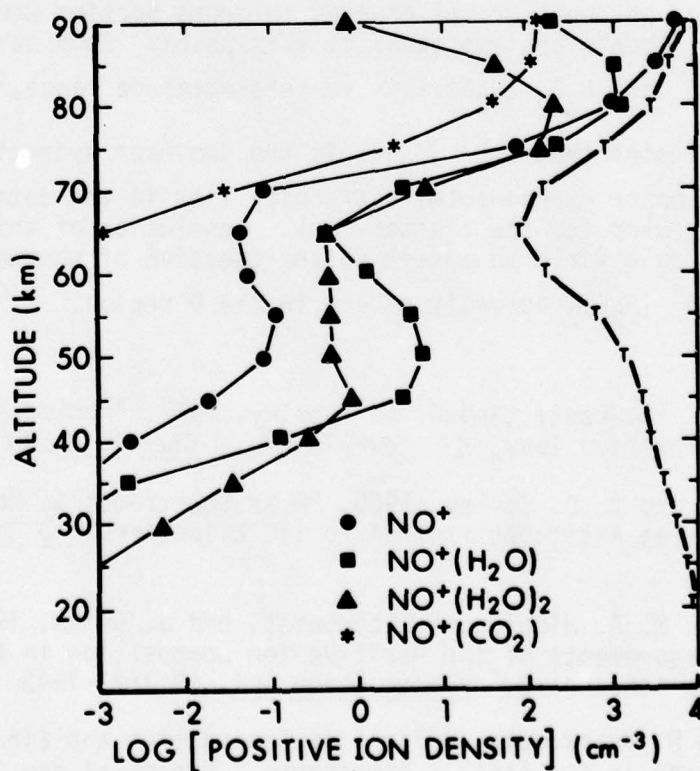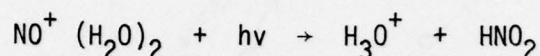

Figure 4. Computed positive ion density profiles for species that have H_3O^+ as their core ion. The total positive ion profile is given by the heavy curve marked "T."

One point to be noted is that the code predicts H_3O^+ (H_2O) to be the dominant hydronium ion in the 80 to 90 km region. This prediction is because of the proposed reaction

$$NO^+ (H_2O)_2 + h\nu \rightarrow H_3O^+ + HNO_2$$

and the subsequent hydration of the H_3O^+. Attempted measurements[23] of the photon absorption cross section of NO^+ $(H_2O)_2$ have indicated that it is below the detection threshold of $10^{-20} cm^2$. However, our modeling calculations show that the above reaction forms a link between NO^+ and H_3O^+ even when a cross section as small as $2 \times 10^{-21} cm^2$ is assumed. Specifically, at 80 km the ratio of H_3O^+ $(H_2O)_2/H_3O^+$ (H_2O) as computed from the model is 0.06, 1.3, and 12 for photodestruction cross sections of $2 \times 10^{-19} cm^2$, $2 \times 10^{-21} cm^2$, and 0.0 cm^2, respectively. Therefore, relative ratio of the hydrates of H_3O^+ is a sensitive indicator of the importance of the photolysis of NO^+ $(H_2O)_2$ (whereas the total positive ion density varies only a few percent for the changes in cross section used above). Rocket ion measurements are ambiguous at this point. Some have shown an abundance of H_3O^+ and H_3O^+ (H_2O) ions in this altitude range,[11,24] while

others have indicated that H_3O^+ $(H_2O)_2$ is the dominant hydronium ion cluster.[25] The major experimental difficulty lies in the determination of the degree of breakup for the cluster ions. Resolution of this experimental problem could yield an answer to the question of whether the photolysis of NO^+ $(H_2O)_2$ actually occurs in the D region.

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[23]G. P. Smith, P. C. Cosby, and J. T. Moseley, 1977, "Photodissociation of Atmospheric Positive Ions, I: 5300-6700Å, J Chem Phys, 67:3818-3828

[11]R. S. Narcisi and A. D. Bailey, 1965, "Mass Spectrometric Measurements of Positive Ions at Altitudes from 64 to 112 Kilometers," J Geophys Res, 70:3687-3700

[24]P. A. Zbinden, M. A. Hidalgo, P. Eberhardt, and J. Geiss, 1975, "Mass Spectrometer Measurements of the Positive Ion Composition in the D and E Regions of the Ionosphere," Planet Space Sci, 23:1621-1642

[25]F. Arnold and D. Krankowsky, 1977, "Ion Composition and Electron and Ion Loss Processes in the Earth's Atmosphere," Dynamical and Chemical Coupling, 93-127, B. Grandal and J. Holtet, eds., Dr. Reidel, Dordrecht

Figure 5 illustrates the summed profiles for the two main ion groupings -- the one with NO^+ as the core ion and the other with the H_3O^+ as the core ion. The crossover point between the two groupings is 75 km, which is in reasonable agreement with experimental observations. Figure 5 shows that the region of 60 to 75 km, where the simulated total positive ion profile is less than the experimentally determined one (see figure 2), is clearly dominated by H_3O^+ cluster ions. As mentioned in the previous section, one possible reason for the lower simulated ion densities is that the effective recombination rate may be too large. This large recombination rate may in turn have two causes. One cause may be that the code predicts multiple-cluster ions which are larger (in mass) than the ones which were actually present. If the dominant cluster ion were $H_3O^+ (H_2O)$ rather than the predicted $H_3O^+ (H_2O)_3$, the electron ion recombination coefficient would be half as large. Nominally this would increase both the ion and electron densities approximately 40 percent, which would improve the comparison between the ion profiles but increase the discrepancy between the electron profiles. Other experimental determinations of exact ion composition are still subject to interpretation. Some measurements[20,24] indicate that $H_3O^+ (H_2O)$ may be the predominant positive ion in the lower D region, while other experiments[11,25] show that the heavier clusters dominate. Until the question of cluster breakup is resolved, we adopt the position that the code correctly predicts the heavier positive ion clusters. The other cause of a too-large effective recombination rate may be in the negative ion concentrations and negative ion to electron ratio. As a "rule-of-thumb," the ion-ion recombination coefficients are one to two orders of magnitude smaller than electron-ion recombination

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[20]R. S. Narcisi, A. D. Bailey, L. E. Wlodyka, and C. R. Philbrick, 1972, "Ion Composition Measurements in the Lower Ionosphere During the November 1966 and March 1970 Solar Eclipses," J Atmos Terr Phys, 34:647-658

[24]P. A. Zbinden, M. A. Hidalgo, P. Eberhardt, and J. Geiss, 1975, "Mass Spectrometer Measurements of the Positive Ion Composition in the D and E Regions of the Ionosphere," Planet Space Sci, 23:1621-1642

[11]R. S. Narcisi and A. D. Bailey, 1965, "Mass Spectrometric Measurement of Positive Ions at Altitudes from 64 to 112 Kilometers," J Geophys Res, 70:3687-3700

[25]F. Arnold and D. Krankowsky, 1977, "Ion Composition and Electron and Ion Loss Processes in the Earth's Atmosphere," Dynamical and Chemical Coupling, 93-127, B. Grandal and J. Holtet, eds., Dr. Reidel, Dordrecht
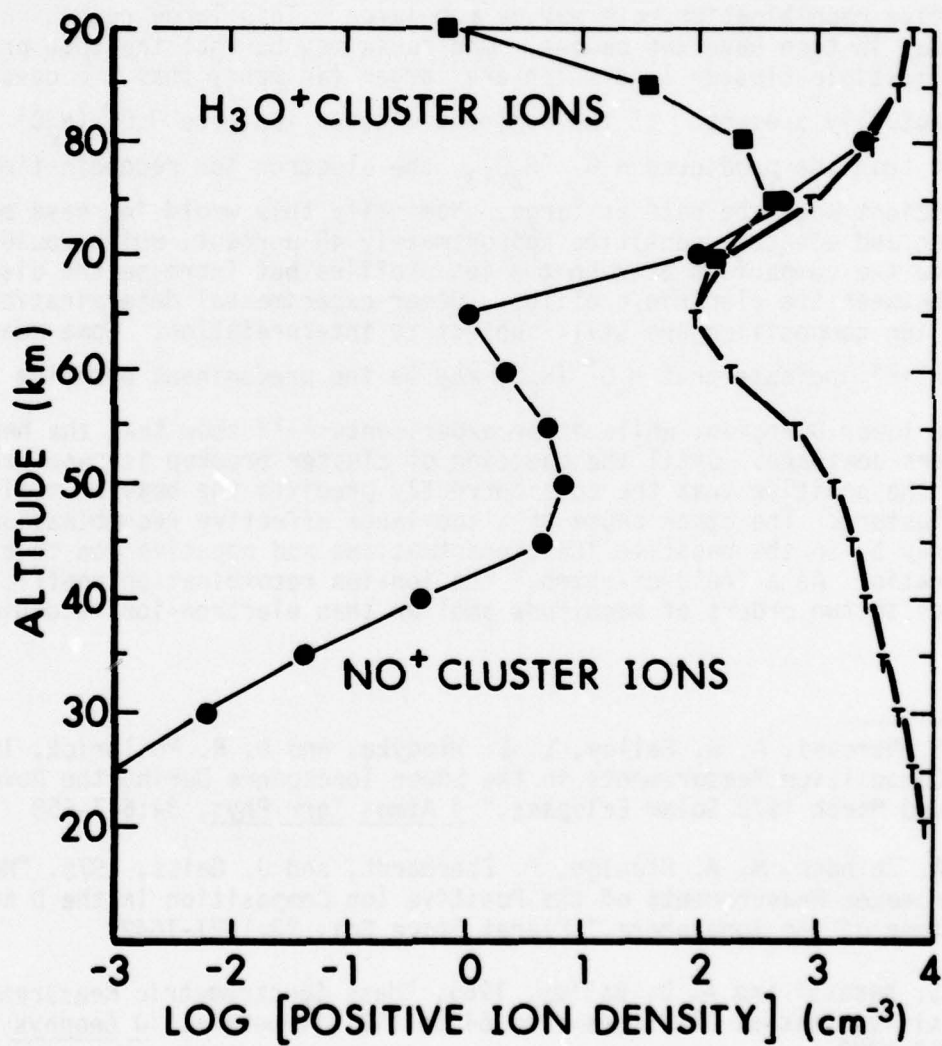
Figure 5. NO$^+$ cluster ions and H$_3$O cluster ions represent the sums of the profiles of figures 3 and 4, respectively. Below 65 km the total positive ions are very well approximated by the H$_3$O$^+$ core cluster ions, above 85 km by the NO$^+$ core cluster ions.

coefficients.[26,27] Thus, an appreciable concentration of negative ions in the 60 and 75 km region would increase the simulated positive ion densities and thus improve the agreement of the two positive ion profiles in figure 2, while also possibly reconciling some of the differences between the simulated and experimentally determined electron profiles. This idea will be explored further in the next section.

NEGATIVE ION CHEMISTRY

The major formation process for the initial negative ion is the three-body attachment of electrons to O_2

$$e + O_2 + M \rightarrow O_2^- + M.$$
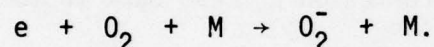
However, there are also rapid detachment processes for O_2^-

$$O_2^- + O \rightarrow O_3 + e,$$

$$O_2^- + O_2\left({}^1\Delta_g\right) \rightarrow 2O_2 + e,$$
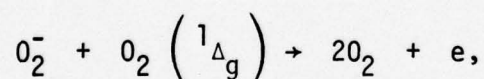
which tend to limit the O_2^- density in the upper D region. The next important step in the formation of more complex and stable negative ions is a charge exchange reaction between O_3 and O_2^-

$$O_2^- + O_3 \rightarrow O_3^- + O_2,$$

[26]D. Smith, N. G. Adams, and M. J. Church, 1976, "Mutual Neutralization Rates of Ionospherically Important Ions," Planet Space Sci, 24:697-703

[27]D. Smith and M. J. Church, 1977, "Ion-Ion Recombination Rates in the Earth's Atmosphere," Planet Space Sci, 25:433-439

followed by the reaction

$$O_3^- + CO_2 \rightarrow CO_3^- + O_2.$$

The CO_3^- ion, however, is also dissociated by atomic oxygen

$$CO_3^- + O \rightarrow O_2^- + CO_2$$

which short circuits the negative ion formation process back to the O_2^- ion. The next major step is the reaction

$$CO_3^- + NO \rightarrow NO_2^- + CO_2$$

which is followed by the reaction

$$NO_2^- + O_3 \rightarrow NO_3^- + O_2$$

to form the negative ion with the largest electron affinity, NO_3^-.

The major paths along which the charge flows are illustrated in figure 6. Although there are numerous other reactions which enter in, the main sequence has been outlined above. Of interest is the secondary path of O_2^- clustering to form O_4^- which in turn switches with CO_2 to form CO_4^-. While this is not a major path for the flow of charge, appreciable buildup of the CO_4^- ion can occur because of its small photodissociation cross section.[28,29] Hydration reactions occur for essentially all of the

[28]G. P. Smith, L. C. Lee, P. C. Cosby, J. R. Peterson, and J. T. Moseley, 1978, "Photodissociation and Photodetachment of Molecular Negative Ions, V: Atmospheric Ions from 7000 to 8400 Å," J Chem Phys, 68:3818-3822

[29]M. L. Vestal and G. H. Mauclaire, 1977, "Photodissociation of Negative Ions Formed in CO_2 and CO_2/O_2 Mixtures," J Chem Phys, 67:3758-3766

70 KM

NEGATIVE ION FLOW CHART

Figure 6. Major paths for flow of negative charge down the negative ion chain. Solid boxes indicate ions with appreciable concentrations; dashed-line boxes indicate important intermediary ions which have very small concentrations.

negative species, with hydrated forms of the ions expected to be dominant at lower altitudes. Chemical considerations indicated that nitric acid, HNO_3, will replace water in the NO_3^- core ion clusters in the stratosphere.[30,31]

The negative ion chemistry as it is currently understood may be divided into conveniently separable phases. The initial entry into the negative ion chain is through the three-body attachment of electrons to O_2. The major negative ions, which also serve as core ions for clusters, are O_2^-, CO_3^-, and NO_3^-. Atomic oxygen is the major inhibitor of charge flow down the chain because it attacks both O_2^- and CO_3^-. Ozone is the major expeditor of flow down the chain by bridging the gaps from O_2^- to CO_3^- and then, with the aid of NO, to NO_3^-. Clustering becomes important as one descends in altitude and cluster ions will be the dominant form of ion in the lower mesosphere and throughout the stratosphere.

The computer code simulations of the negative ion densities are illustrated in the set of figures 7 through 10. Figure 7 shows the altitude profiles for those ions which have O_2^- as their core ion. The figure also shows the O^- ion density profile since a major source of O^- is charge exchange with O_2^-. O^- and O_2^- are predicted to be the major negative ions in the upper D region, although in terms of the total charge they are minor negative species. CO_4^- is considered to be an O_2^- core ion cluster; and CO_4^- and its water cluster follow the O_2^- profile very well in the 65 to 40 km region. Below 40 km, three-body clustering reactions become so efficient that CO_4^- and its hydrate actually begin to increase at the expense of the simpler O_2^- ion. Figure 8 shows the altitude profiles of the CO_3^- ion and its water cluster. The CO_3^- density once again follows the O_2^- rather closely, but decreases less rapidly than the O_2^- density in the stratosphere due to the increasing ratio of ozone as one descends in altitude in this region. CO_3^- is computed to be the most abundant negative ion in the 60 and 65 km region. NO_3^- rapidly becomes the dominant negative ion below 60 km as is shown in figure 9, with its clusters of water and nitric acid becoming

[30]F. C. Fehsenfeld, C. J. Howard, and A. J. Schmeltekopf, 1973, "Gas Phase Ion Chemistry of HNO_3," _J Chem Phys_, 63:2835-2841

[31]J. C. Harris, D. G. Moos, N. R. W. Swann, G. F. Neill, and P. Gildwarg, 1976, "Simultaneous Measurements of H_2O, NO_2, and HNO_3 in the Daytime Stratosphere from 15 to 35 km," _Nature_, 259:300-301
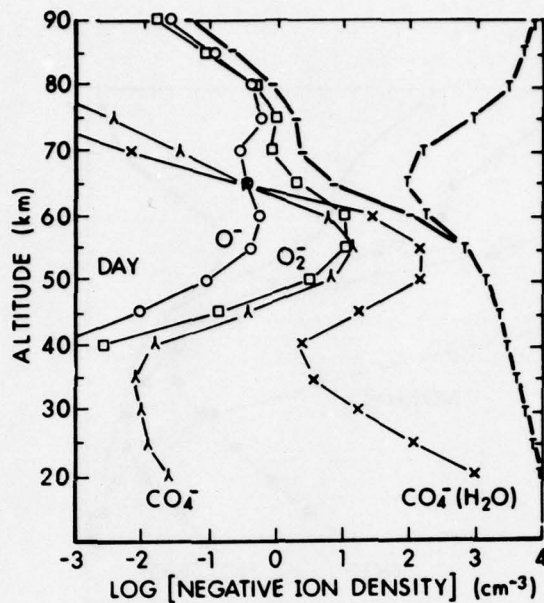
Figure 7. Profiles of negative ions that have O_2^- as their core; CO_4^- is taken to be $O_2^- (CO_2)$. O profile is also shown. The total positive ion profile is given by the heavy line marked "T." Above 55 km the total negative ion profile is shown by "-." Below 55 km the total positive and total negative profiles overlap.

Figure 8. Profiles of the negative ions that have CO_3^- as their core ion. The total negative ion profile is shown by the heavy line marked "-" above 55 km and "T" below 55 km.
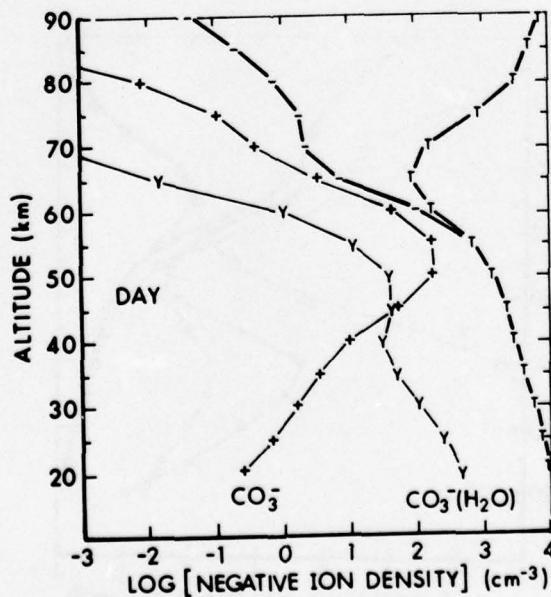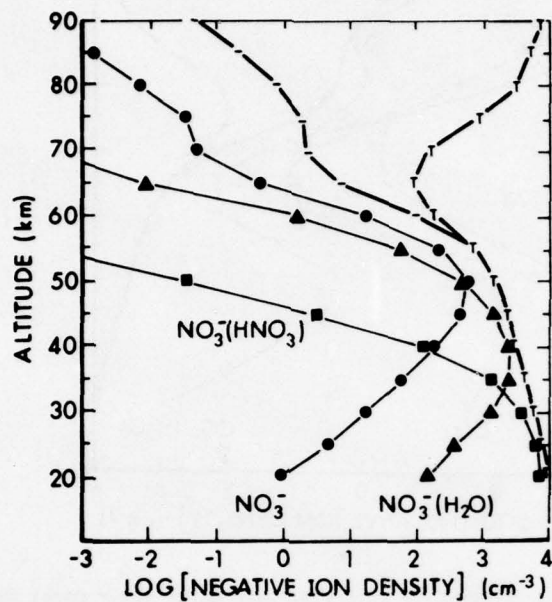
Figure 9. Profiles of the negative ions that have NO_3^- as their core ion. The total negative ion profile is shown by the heavy line marked "-" above 55 km and "T" below 55 km.
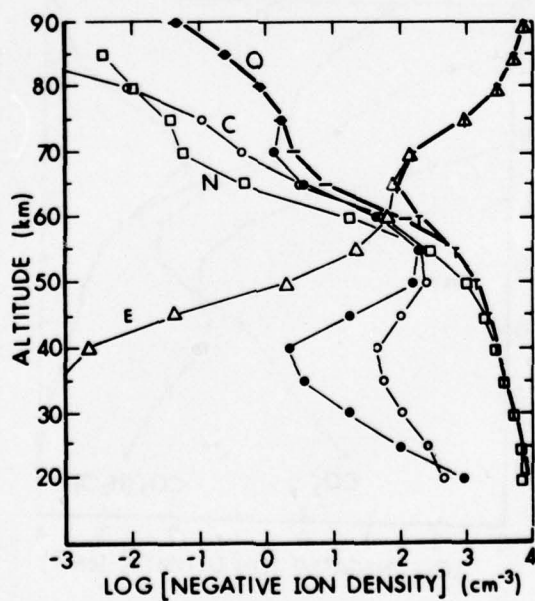

Figure 10. O, C, and N represent the profiles of the sums of the negative ions that are given in figures 7, 8, and 9, respectively. The electron density profile, E, is also shown.

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the more important ions in the stratosphere. Only one molecule each of water and nitric acid were clustered to NO_3^- in this model. More complex and mixed clusters have not been included at the present but most probably do exist in nature.

Figure 10 shows the three groups of negative ions, O_2^-, CO_3^- and NO_3^-, and the total charge. These groupings do not show the sharp distinctions with altitude that the NO^+ and H_3O^+ groups did in figure 5, but the transitions from O_2^- to CO_3^- to NO_3^- groupings are still apparent as one descends in altitude. Table 1 lists the dominant positive and negative species and their corresponding altitude ranges. Certain features should be noted when figures 5 and 10 are compared. First, clustering to positive ions is an important process throughout the entire D region, whereas clustering to negative ions only becomes dominant below 60 km. Secondly, the total negative ion density quickly decreases above 60 km. These features are due mainly to the fact that the negative ions O_2^- and CO_3^- are attacked by atomic oxygen, whose density increases with altitude, and to the fact that the formation of the more stable negative ions depends on ozone, whose density decreases with altitude. The DAIRCHEM computer code therefore predicts small negative ion densities in the D region.

Comparison of the code's predictions with available experimental data is somewhat disquieting. Mass spectrometer measurements have indicated the presence of negative ions throughout the D region,[32,33,20] although the absolute concentrations are still in question. Rapid decreases in the negative ion density with increasing altitude have been observed in the vicinity of 78 and 90 km, whereas the code predicts that the negative ion density begins to decrease above the much lower altitude of 60 km. The presence of heavy negative ion clusters, often with masses greater than 150 u, has been experimentally inferred in the 70 to 90 km region.[20,32]

The code predicts only the simple negative ions, O_2^-, O^-, CO_3^-, and NO_3^-,

[32]R. S. Narcisi, A. D. Bailey, L. Della Lucca, C. Sherman, and D. M. Thomas, 1971, "Mass Spectrometric Measurements of Negative Ions in the D and Lower E Regions," J Atmos Terr Phys, 33:1147-1159

[33]F. Arnold, J. Kissle, D. Krankowsky, H. Wieder, and J. Zähringer, 1971, "Negative Ions in the Lower Ionosphere: A Mass Spectrometric Measurement," J Atmos Terr Phys, 33:1169-1175

[20]R. S. Narcisi, A. D. Bailey, L. E. Wlodyka, and C. R. Philbrick, 1972, "Ion Composition Measurements in the Lower Ionosphere During the November 1966 and March 1970 Solar Eclipses," J Atmos Terr Phys, 34:647-658

TABLE 1.   QUIET TIME D REGION

Altitude Range (km)	Dominant Negative Ion	Dominant Positive Ion
85-90	O^-	NO^+
80-85	O_2^- , O^-	$NO^+(H_2O)$, NO^+
75-80	O_2^-	$H_3O^+(H_2O)_n$, $NO^+(H_2O)$
70-75	O_2^-	$H_3O^+(H_2O)_n$
65-70	CO_3^- , O_2^-	"
60-65	CO_3^-	"
55-60	NO_3^- , CO_3^-	"
50-55	NO_3^-	"
40-50	$NO_3^-(H_2O)$, NO_3^-	"
30-40	$NO_3^-(HNO_3)$, $NO_3^-(H_2O)$	"
20-30	$NO_3^-(HNO_3)$	"

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in this region. The electron and total positive ion density profiles shown
in figure 2, which were derived from independent rocket measurements, imply
an increasing negative ion density in the 60 and 85 km region which equals
and even exceeds the electron density. Again the known ion chemistry pre-
dicts a decreasing negative ion density in this region.

It has become evident at this point that, in contrast to the positive ion
chemistry, there are several major uncertainties in connection with the
negative ion chemistry and the resultant electron and negative ion den-
sities. Several suggestions can be made which may help to reconcile or
at least better define the current uncertainties.

When the rocket measurements yielding the data shown in figure 2 were made,
there were no simultaneous measurements of ozone and atomic oxygen made.
Considering the importance of these minor neutral species in the formation
of negative ions, detailed profiles in the 60 to 90 km region would be
helpful. The DAIRCHEM code does determine representative $[O_3]$ and $[O]$

profiles based on time-dependent photochemical considerations, so that the
major effects are already accounted for. Detailed comparisons with experi-
mental profiles would help to resolve questions concerning the exact alti-
tudes of negative ion formation, but would not resolve major discrepancies
involving total negative ion concentrations.

The comparison of computer code results and experimental data would strongly
imply that there is another method of negative ion formation other than the

known three-body attachment of electrons to O_2. The difference between the

measured electron and total positive ion densities in figure 2 also suggests
that a negative species not currently modeled is present in the D region.
The presence of ice particulates of submicron size has been suggested[34]
as a means of providing an alternate electron attachment mechanism and
negative species. Analysis[35] and modeling[36] of data from the 1966 solar
eclipse have yielded similar conclusions.[37] The previously mentioned

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[34]E. T. Chesworth and L. C. Hale, "Ice Particulates in the Mesosphere,"
1974, Geophys Res Letters, 1:347-350

[35]R. D. Sears, 1972, "Analysis of the 1966 Solar Eclipse Data," LMSC
D246526 (DNA 2863F), Lockheed, Palo Alto Research Laboratory

[36]M. G. Heaps, F. E. Niles, and R. D. Sears, 1978, "Modeling the Ion
Chemistry of the D Region: A Case Study Based Upon the 1966 Total Solar
Eclipse," ASL-TR-0015, Atmospheric Sciences Laboratory, White Sands Missile
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[37]M. G. Heaps, "Inclusion of Small Particulates to Explain Variations of
D Region Electron Densities Observed During a Solar Eclipse," ASL-TR
(in preparation)

measurements of heavy negative ions also lend indirect support to the possible role of small particulates in D region processes. An area of further study would be electron attachment/detachment processes, ion clustering and growth mechanisms, and the influence of nongas-phase chemistry in the lower ionosphere.

CONCLUSION

The positive ion chemistry portion of the DAIRCHEM computer code may be considered to be validated by this comparison. In need of further study are electron attachment/detachment processes and the possible role of particulates in D region ion chemistry.

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